PUB-NO: JP408104538A
DOCUMENT-IDENTIFIER: JP 08104538 A
TITLE: HIGH ULTRAVIOLET TRANSMISSION FLUOROPHOSPHATE GLASS AND ITS PRODUCTION

PUBN-DATE: April 23, 1996

INVENTOR-INFORMATION:

NAME	COUNTRY
SUU, GAKUROKU	
TORATANI, HISAYOSHI	

INT-CL (IPC): C03 C 4/00; C03 C 3/247

ABSTRACT:

PURPOSE: To produce a fluorophosphate glass exhibiting sufficiently high transmission even in an UV ray region of ≤350nm wavelength and having optical homogeneity.

CONSTITUTION: Ions of P, Al, Y, Mg, Ca, Sr and Ba are incorporated as a cation, and incorporated in a range of, by mol%, 0.15-20% P ion, 22-40% Al ion, 4-15% Y ion, 3-12% Mg ion, 14-30% Ca ion, 7-16% Sr ion and 4-20% Ba ion and O ion and F ion are incorporated as an anion, and incorporated in the range of, by mol%, 0.5-27% O ion, 73-99.5% F ion, moreover, OH ion is incorporated. An atmosphere for melting glass is gaseous mixture of inert gas and steam, and the glass containing hydroxide, etc., is used as a starting material.

End of Result Set

Generate Collection | Print

L1: Entry 2 of 2 File: DWPI Apr 23, 1996

DERWENT-ACC-NO: 1996-254992
DERWENT-WEEK: 199626

TITLE: High UV transmitting fluorine phosphate glass - contg. aluminium, yttrium, magnesium, calcium, strontium and barium cations

PRIORITY-DATA: 1994JP-0238783 (October 3, 1994)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE	PAGES	MAIN-IPC
JP 08104538 A	April 23, 1996		011	C03C004/00

INT-CL (IPC): C03 C 3/247; C03 C 4/00

ABSTRACTED-PUB-NO: JP 08104538A
BASIC-ABSTRACT:

P, Al, Y, Mg, Ca, Sr and Ba are included are a cation of a glass, and O and F are included as an anion. An OH ion is further included.

ADVANTAGE - Transmissivity to UV below 350 nm wavelength.

X 1-3 B Ex29

(19)日本国特許庁（ＪＰ）　　(12) 公開特許公報（Ａ）　　(11)特許出願公開番号

特開平8－104538

(43)公開日　平成８年(1996)４月23日

(51)Int.Cl.⁶	識別記号	庁内整理番号	ＦＩ	技術表示箇所
ＣＯ３Ｃ　4/00				
3/247				

審査請求　未請求　請求項の数４　ＯＬ　（全 11 頁）

(21)出願番号　特願平6－238783

(22)出願日　平成６年(1994)10月３日

(71)出願人　000113263
ホーヤ株式会社
東京都新宿区中落合２丁目７番５号

(72)発明者　鄒　学禄
東京都新宿区中落合２丁目７番５号　ホーヤ株式会社内

(72)発明者　虎渓　久良
東京都新宿区中落合２丁目７番５号　ホーヤ株式会社内

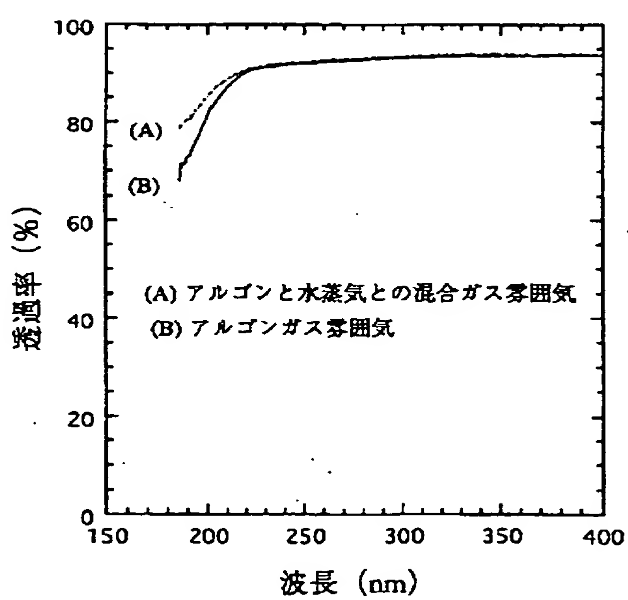
(74)代理人　弁理士　塩澤　寿夫　（外１名）

(54)【発明の名称】　高紫外線透過性弗燐酸塩ガラス及びその製造方法

(57)【要約】　　（修正有）

【目的】　波長３５０ｎｍ以下の紫外線領域でも十分に高い透過性を示し、かつ光学的均質性を有する弗燐酸塩ガラス及びその製造方法の提供。

【構成】　陽イオンとして、Ｐ、Ａｌ、Ｙ、Ｍｇ、Ｃａ、Ｓｒ及びＢａを含み、モル％で表示して、Ｐイオンが０．１５－２０％、Ａｌイオンが２２－４０％、Ｙイオンが４－１５％、Ｍｇイオンが３－１２％、Ｃａイオンが１４－３０％、Ｓｒイオンが７－１６％、Ｂａイオンが４－２０％の範囲であり、陰イオンとして、Ｏイオンとｆイオンとを含み、モル％で表示して、Ｏイオンが０．５－２７％、Ｆイオンが７３－９９．５％の範囲であり、さらにＯＨイオンを含む。ガラスの溶解雰囲気を不活性ガスと水蒸気との混合ガスとするか、水酸化物等を含むガラスを原料とする製造方法より成る。



善に対しては、このような結合をガラス構造から除去することが最大のポイントとなると推察し、種々検討を行った。その結果、比較的少量の燐酸を含有するガラスに少量ＯＨイオンを導入することで、ガラス構造中のＰ−Ｏ−Ｒ結合をＰ−Ｏ−Ｈ結合で置き換えた少量ＯＨドープ弗燐酸塩ガラスが、今までにない優れた紫外線透過性を有し、かつ光学的均質性を有することを見出して本発明を完成した。

【０００６】本発明は、ガラスを構成する陽イオンとして、Ｐ、Ａｌ、Ｙ、Ｍｇ、Ｃａ、Ｓｒ及びＢａを含み、前記各陽イオンの割合がモル％で表示して、Ｐイオンが０．１５−２０％の範囲、Ａｌイオンが２２−４０％の範囲、Ｙイオンが４−１５％の範囲、Ｍｇイオンが３−１２％の範囲、Ｃａイオンが１４−３０％の範囲、Ｓｒイオンが７〜１６％の範囲、Ｂａイオンが４−２０％の範囲であり、且つガラスを構成する陰イオンとして、Ｏイオンと Ｆイオンとを含み、前記各陰イオンの割合がモル％で表示して、Ｏイオンが０．５−２７％の範囲、Ｆイオンが７３−９９．５％の範囲であり、さらにＯＨイオンを含み、波長3μm付近のＯＨイオンにもとづく吸収ピークの吸収係数α（cm^{-1}）からＣ（cm^{-3}）$=\alpha\times10^{19}$で算出されるＯＨ濃度が$0.04-3\times10^{19}/cm^3$の範囲であることを特徴とする紫外線透過性弗燐酸塩ガラスに関する。

【０００７】さらに本発明は、ガラス原料を溶解し、得られたガラス融液を冷却してガラスを製造する方法であって、前記ガラス原料の溶解雰囲気を不活性ガスと水蒸気との混合ガス雰囲気とすることを特徴とする前記本発明のＯＨイオンを含有する弗燐酸塩ガラスの製造方法、及びガラス原料を溶解し、得られたガラス融液を冷却してガラスを製造する方法であって、ガラス原料として５％以下の水酸化物又は水を含有する化合物を含む混合物を用いることを特徴とする前記本発明のＯＨイオンを含有する弗燐酸塩ガラスの製造方法に関する。

【０００８】尚、本発明の弗燐酸塩ガラスは、ＯＨイオンを導入したことにより、ガラスの紫外線透過率だけでなく、ガラスの失透に対する安定性も向上した。図１に示したように（AlF_4）。の鎖状構造からなる弗化物ガラスにＰイオンとＯＨイオンを導入することによって、

Ｐ−Ｏ−Ｈ−−−Ｆ−Ａｌ−

のような強い水素結合が形成され、（AlF_4）。の鎖状構造３次元的に結合するため、ガラスの結晶化が抑制されるものと考えられる。本発明のガラスの各成分について以下に説明する。

【０００９】Ｐイオンは、ガラス形成酸化物として働き、ガラス構造の安定化即ち失透に対する安定性を増す成分である。また化学的耐久性を向上させるためにもＰイオンは不可欠な成分である。さらにＰイオンは他の陽イオンに比べ優先的にＯＨイオンと結合する特性をもつので、Ｐイオンを弗化物ガラス導入することによってガラス中にあるＯＨイオンのほとんどがＰ−Ｏ−Ｈのように結合される。このような結合はＡｌ−Ｏ−Ｈのような結合に比べ、ガラスの紫外線透過率の向上に寄与することが本発明者らの実験で確認された。ただし、Ｐイオンはガラスの成分として２０％よりも多くなると、紫外線の透過率を低下させるＰ−Ｏ−Ｒのような結合が相対的に多くなるので、得られたガラスの紫外線透過率が悪化する。これに対し、Ｐイオンの含有量が０．５％より少ないとガラスの失透に対する安定性が悪くなり、化学的耐久性も低下してしまう。従って、Ｐイオンの組成範囲は、０．５−２０％の範囲であることが適当である。特に、１−１９％の範囲であることが好ましい。

【００１０】Ａｌイオンはガラスの高紫外線透過率の性質を付与する成分としても、Ｐイオンと共にガラス構造の安定化及びガラス融液の粘性を高め化学的耐久性の向上に寄与する成分としても非常に重要である。ガラスに高紫外線透過率の光学特性を付与するためにも、失透に対する安定性を向上させるためにも２２％以上が必要である。しかし、４０％を超えると逆に失透しやすくなる。従って、Ａｌイオンの組成範囲は、２２−４０％の範囲であることが適当である。特に、２３−３８％の範囲であることが好ましい。

【００１１】Ｙイオンはガラスの失透に対する安定性や屈折率及び化学的耐久性の向上に寄与する成分である。但し、適量範囲を超えて導入するとかえって失透しやすくなるので、４−１５％の範囲であることが適当である。特に、５−１３％の範囲であることが好ましい。

【００１２】Ｍｇイオンはガラスの紫外線透過率を高めるには非常に有用な成分である。但し、１２％を超えるとガラスの失透に対する安定性が低くなり、３％より少ないとガラスの高温溶解性が悪くなるので、３−１２％の範囲が適当である。特に、４−１０％の範囲であることが好ましい。

【００１３】Ｃａイオンはガラスに高紫外線透過率を付与すると共に、失透に対して安定なガラス化範囲を広げるのに有効な成分である。但し、３０％を超え、或いは１４％未満ではガラスの失透に対する安定性が低下するので、１４−３０％の範囲であることが適当である。特に、１４．５−２８％の範囲であることが好ましい。

【００１４】アルカリ土類金属の中でＳｒ、Ｂａのような原子番号の比較的大きなイオンは、いずれもガラスの失透に対する安定性と屈折率を向上させるために導入される成分である。但し、ＳｒイオンとＢａイオンの導入量は、それぞれ１６％及び２０％を超えるとガラスの失透に対する安定性が悪化するのに対し、７％及び４％未満では高温溶解性が悪くなり、十分安定なガラスも得られない。従って、ＳｒイオンとＢａイオンの導入量はそれぞれ７−１６％及び４−２０％の範囲であることが適当である。特に、Ｓｒイオンは８−１５％、Ｂａイオン

注意が必要である。また、ガラスの溶解雰囲気としては、上記（1）の方法では不活性ガスと水蒸気との混合ガスを用い、上記（2）の方法では不活性ガスを用いる。不活性ガスは前記のものである。不活性ガスを用いることで、ガラス中の弗素及びOHの揮発を防ぐためであり、溶解雰囲気からOHイオンをガラスに混入させるためでもある。

【0023】

【発明の効果】本発明のOHドープ弗燐酸塩ガラスは、今までにない優れた紫外線透過性を持ち、またガラスとしても比較的安定に得ることができる。そのため、工業的規模での生産が可能であり、石英ガラス及びCaF_2結晶に代わる光学材料として非常に有望である。さらに、光学機器に用いられる光学部品としても、紫外線光、可視光伝送用ファイバの母材としても有望である。特に、0．2以上大きい開口数を有する紫外線伝送用ファイバの作成に有用である。

【0024】

【実施例】以下、本発明をさらに説明するが、本発明はこれらの実施例に限定されるものではない。

実施例1～36

表1～表3には実施例のガラス組成を陽イオン及び陰イオンの割合を示し、表4～表6には表1～表3に示した組成に対応する各種化合物の割合をモル％で示した。これらのガラスを溶解する際の出発原料としては、$Al(PO_3)_3$、$Mg(PO_3)_2$、$Ca(PO_3)_2$、$Sr(PO_3)_2$、$Ba(PO_3)_2$、H_3PO_4、$Al(OH)_3$、$Mg(OH)_2$、$Ca(OH)_2$、$Sr(OH)_2$、$Ba(OH)_2$、AlF_3、YF_3、MgF_2、CaF_2、SrF_2、BaF_2、 NaF、LiF及びKFなどを用いた。これらの原料を、表4～6に示した所定の割合に50～100g秤取し、十分混合して調合原料と成した。得られた調合原料をカーボンるつぼに入れ、950～1100℃でアルゴンと水蒸気との混合ガス雰囲気で1～2時間ガラスの溶解を行った。熔融後、ガラス融液をカーボンるつぼに入れたまま室温まで放冷してガラスを得た。得られたガラスは無色透明で光学顕微鏡で観察できる結晶は析出していなかった。

【0025】ガラス中へのOHイオンの導入は、ガラス溶解雰囲気への水蒸気の導入又は原料への水酸化物及び／又は結晶水を含む化合物の混合（又はその両方）により行った。水蒸気の導入については、アルゴンガスを洗浄瓶の中の水蒸気で飽和させ、ある程度の水蒸気分圧を得てからこの混合ガスを溶解炉に供給し、ガラス溶解の雰囲気とした。溶解炉雰囲気の水蒸気分圧は、図3に示す洗浄瓶中の水の温度で調整し、これを通じてガラス中のOHイオンの含有量を調整した。例えば、洗浄瓶の水の温度を25、45、85℃とした水蒸気分圧の混合雰囲気で溶解した実施例26、27、28のガラス中のOHイオンの濃度は、それぞれ0．21、0．46、0．88$\times 10^{19}$／cm^3 となった。その他、実施例1、2、4、7、11、12、13、14、15、16、17、18、20、23、24、26、27、29、34、35、36は溶解雰囲気中への水蒸気の導入によりOHイオンの導入を行った。また、実施例30、32は、原料への水酸化物の混合によりOHイオンの導入を行った。さらに、実施例3、5、6、8、9、10、19、21、22は、溶解雰囲気中への水蒸気の導入及び原料への水酸化物の混合によりOHイオンの導入を行った。各ガラスのOHイオン含有量は表1～3に示す。

【0026】

【表1】

実施例番号	13	14	15	16	17	18	19	20	21	22	23	24
陽イオン%												
Pイオン	2.99	2.99	2.99	2.99	2.99	4.14	4.14	4.98	4.98	4.98	4.98	4.98
Alイオン	38.32	35.33	35.33	35.33	31.02	35.48	35.48	34.92	34.92	34.92	34.92	34.93
Yイオン	5.72	8.71	8.71	8.71	14.50	8.65	8.65	8.61	8.61	8.61	8.61	8.61
Mgイオン	4.73	5.15	3.45	10.06	6.59	6.62	6.62	6.59	6.59	6.59	6.09	6.09
Caイオン	19.82	16.83	28.77	26.30	23.61	23.73	23.73	23.61	23.61	23.61	23.61	23.61
Srイオン	13.75	14.99	10.04	11.89	11.55	11.61	11.61	11.55	11.55	11.55	11.55	11.55
Baイオン	14.68	16.01	10.72	4.74	9.74	9.79	9.79	9.74	9.74	9.74	9.24	8.74
Liイオン	—	—	—	—	—	—	—	—	—	—	1.00	—
Naイオン	—	—	—	—	—	—	—	—	—	—	—	1.50
Kイオン	—	—	—	—	—	—	—	—	—	—	—	—
陰イオン%												
Oイオン	3.67	3.67	3.67	3.67	3.67	5.09	5.09	6.13	6.13	6.13	6.14	6.15
Fイオン	96.33	96.33	96.33	96.33	96.33	94.91	94.91	93.87	93.87	93.87	93.86	93.85
OH(10[illegible]/cm^3)	0.15	0.16	0.17	0.15	0.15	0.18	0.41	0.19	0.41	0.92	0.18	0.19
透過率(200nm)	86.0	86.0	86.0	86.0	86.0	—	—	84.0	84.0	83.0	84.0	84.0

【0028】

【表3】

実施例番号	25	26	27	28	29	30	31	32	33	34	35	36
陽イオン%												
Pイオン	4.98	6.97	6.97	6.97	10.00	10.00	10.00	10.00	10.00	12.00	15.00	18.00
Alイオン	34.93	33.33	33.33	33.33	31.30	31.30	31.30	31.30	31.30	29.29	26.25	23.52
Yイオン	8.61	8.21	8.21	8.21	6.93	6.93	6.93	6.93	6.93	7.73	7.93	7.93
Mgイオン	6.09	6.59	6.59	6.59	6.32	6.32	6.32	4.32	4.32	3.78	3.78	3.62
Caイオン	23.61	23.61	23.61	23.61	22.73	22.73	22.73	21.73	21.73	16.62	14.86	14.86
Srイオン	11.05	11.55	11.55	11.55	12.91	12.91	12.91	11.91	11.91	10.41	9.71	10.70
Baイオン	9.24	9.74	9.74	9.74	9.79	9.79	9.79	9.29	9.29	18.47	18.47	16.87
Liイオン	—	—	—	—	—	—	—	—	—	—	—	—
Naイオン	—	—	—	—	—	—	—	4.50	—	1.70	4.00	4.50
Kイオン	1.5	—	—	—	—	—	—	—	4.50	—	—	—
陰イオン%												
Oイオン	6.15	8.65	8.65	8.65	12.62	12.62	12.62	12.87	12.87	15.30	19.55	23.79
Fイオン	93.85	91.35	91.35	91.35	87.38	87.38	87.38	87.13	87.13	84.70	80.45	76.21
OH(10[illegible]/cm^3)	0.18	0.21	0.46	0.88	0.23	0.64	2.84	0.74	0.23	0.27	0.31	0.36
透過率(200nm)	84.0	83.0	83.5	82.5	82.0	82.0	79.5	81.5	82.0	81.0	78.5	76.0

【0029】

【表4】

CATION %

実施例番号	25	26	27	28	29	30	31	32	33	34	35	36
PO2.5	4.98	6.97	6.97	6.97	10.00	10.00	10.00	10.00	10.00	12.00	15.00	18.00
AlO1.5	0.995	2.32	2.32	2.32	3.34	3.34	3.34	3.34	3.34	4.00	5.00	5.00
BaO	0.995	—	—	—	—	—	—	—	—	—	—	—
AlF3	33.93	31.01	31.01	30.51	27.96	27.96	23.96	27.96	27.96	25.29	21.25	17.52
YF3	8.61	8.21	8.21	8.21	6.93	6.93	6.93	6.93	6.93	7.73	7.93	7.93
MgF2	6.09	6.59	6.59	6.59	6.32	6.32	6.32	4.32	4.32	3.78	3.78	3.62
CaF2	23.61	23.61	23.61	23.61	22.73	22.73	22.73	21.73	21.73	16.62	14.86	14.86
SrF2	11.05	11.55	11.55	11.55	12.91	12.91	12.91	11.91	11.91	10.41	9.71	10.70
BaF2	8.25	9.74	9.24	9.74	9.79	9.19	9.79	9.29	9.29	18.47	18.47	16.87
LiF	—	—	—	—	—	—	—	—	—	—	—	—
NaF	—	—	—	—	—	—	—	3.00	—	1.70	4.00	4.50
KF	1.50	—	—	—	—	—	—	—	4.50	—	—	—
Al(OH)3	—	—	—	0.50	—	—	4.00	—	—	—	—	—
Ba(OH)2	—	—	—	—	—	0.60	—	—	—	—	—	—
Na(OH)	—	—	—	—	—	—	—	1.50	—	—	—	—

【0032】ガラスの赤外線スペクトル及び紫外線スペクトルの測定は、それぞれ日本電子－330型分光光度計と日本分光VALOR－III型赤外線分光光度計で厚さ10mmのサンプルガラスを用いて行った。ガラス中のOHイオンの濃度は、ガラスの赤外線吸収スペクトルを用い、次の式（Journal of Non－Crystalline Solids，163（1993）p74－80の文献を参照）で定量した。

OH濃度（cm^{-3}）＝α（OH）×10^{19}

ここで吸収係数のα（OH）（cm^{-1}）は吸収スペクトルから次式で計算することができる。

α（OH）＝（1／L_0）×Ln（I_0／I_D）

ここでL_0はサンプルの厚さ、I_0はサンプルの最高透過率（通常は波長1400nmの透過率を用いる）、I_Dは波長3000－3200nm範囲にあるOHイオンの吸収ピークとなる波長での透過率である。

【0033】図4には（A）アルゴンと水蒸気との混合ガス雰囲気で溶解した実施例7のガラスと（B）乾燥したアルゴンガス雰囲気で溶解した同組成のガラス（比較例）の紫外線透過スペクトルを示した。水蒸気を含有する雰囲気で溶解した本発明のガラスの紫外線透過率は、乾燥アルゴンガス雰囲気で溶解した比較例のガラスのそれよりも高いことが図4から分かる。また、石英ガラスと比較するため、図5には市販のSuprasil－P20石英ガラスと実施例14のガラスの紫外線透過スペクトルを示した。本発明のガラスは波長200－400nmの紫外線領域で石英ガラスと同程度或いはそれより少し高い透過率を有することが図5からはっきり分かる。さらに他の実施例のガラスについての紫外線透過性は、表1～3に示す。以上の実施例より本発明のガラスは200～400nm波長範囲の紫外線光用レンズ、窓材、ミラー、フィルターなどの光学材料または紫外線光伝送ファイバ用母材として期待される。

【図面の簡単な説明】

【図1】 （AlF_4）$_n$の鎖状構造からなる弗化物ガラスにP－O－H－－－F－Al－のような強い水素結合が形成されて（AlF_4）$_n$の鎖状構造3次元的に結合することを説明する図。

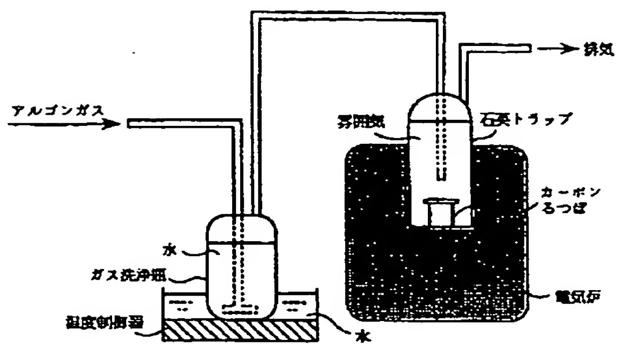
【図2】 OHイオンを含まない失透したガラス（比較例）と、アルゴンと水蒸気との混合ガス雰囲気で溶解したOHイオンを含む透明な本発明のガラスの図面に代わる写真。

【図3】 溶解炉への水蒸気導入のプロセスの概略図。

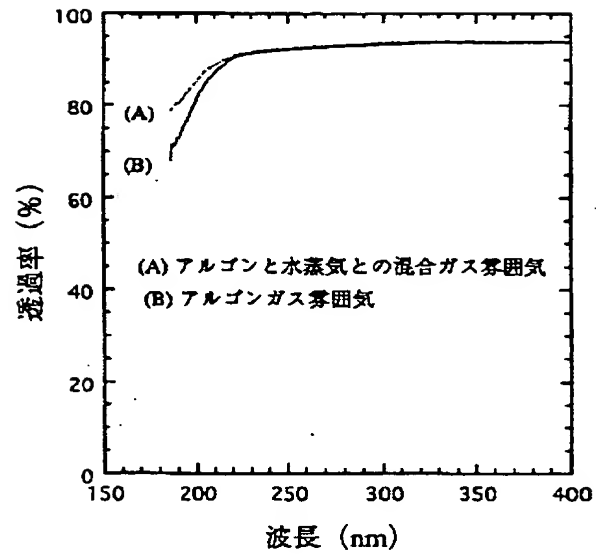
【図4】 （A）アルゴンと水蒸気との混合ガス雰囲気で溶解した実施例7のガラスと（B）乾燥したアルゴンガス雰囲気で溶解した同組成のガラス（比較例）の紫外線透過スペクトル。

【図5】 市販のSuprasil－P20石英ガラスと実施例14のガラスの紫外線透過スペクトル。

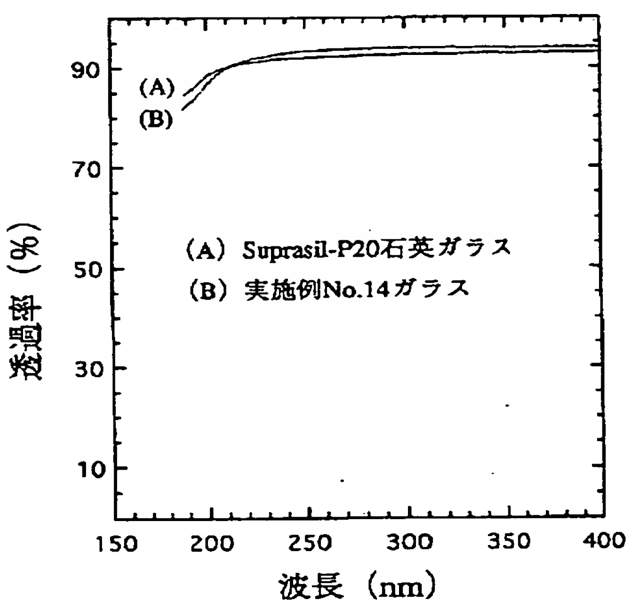
【図３】


アルゴンガス
排気
雰囲気
石英トラップ
カーボン
るつぼ
水
ガス洗浄瓶
温度制御器
水
電気炉

【図４】


100
80
60
40
20
0
150
200
250
300
350
400
(A)
(B)
(A) アルゴンと水蒸気との混合ガス雰囲気
(B) アルゴンガス雰囲気
透過率（%）
波長（nm）

【図５】


90
70
50
30
10
150
200
250
300
350
400
(A)
(B)
（A）Suprasil-P20石英ガラス
（B）実施例No.14ガラス
透過率（%）
波長（nm）

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 08-104538
(43)Date of publication of application : 23.04.1996

(51)Int.Cl. C03C 4/00
C03C 3/247

(21)Application number : 06-238783
(22)Date of filing : 03.10.1994

(71)Applicant : HOYA CORP
(72)Inventor : SUU GAKUROKU
TORATANI HISAYOSHI

(54) HIGH ULTRAVIOLET TRANSMISSION FLUOROPHOSPHATE GLASS AND ITS PRODUCTION

(57)Abstract:
PURPOSE: To produce a fluorophosphate glass exhibiting sufficiently high transmission even in an UV ray region of ≤350nm wavelength and having optical homogeneity.
CONSTITUTION: Ions of P, Al, Y, Mg, Ca, Sr and Ba are incorporated as a cation, and incorporated in a range of, by mol%, 0.15-20% P ion, 22-40% Al ion, 4-15% Y ion, 3-12% Mg ion, 14-30% Ca ion, 7-16% Sr ion and 4-20% Ba ion and O ion and F ion are incorporated as an anion, and incorporated in the range of, by mol%, 0.5-27% O ion, 73-99.5% F ion, moreover, OH ion is incorporated. An atmosphere for melting glass is gaseous mixture of inert gas and steam, and the glass containing hydroxide, etc., is used as a starting material.

LEGAL STATUS

[Date of request for examination] 05.02.2001

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

* NOTICES *

CLAIMS

[Claim(s)]
[Claim 1] As a cation which constitutes glass, the rate of each aforementioned cation displays by mol % including P, aluminum, Y, Mg, calcium, Sr, and Ba. 0.15-20% of range and aluminum ion 22-40% of range, [P ion] Y ion as an anion which 7 - 16% of range and Ba ion are [4-15% of range, and Mg ion / 14-30% of range and Sr ion] 4-20% of ranges for 3-12% of range, and calcium ion, and constitutes glass The rate of each aforementioned anion displays by mol % including O ion and F ion. O ion is 0.5-27% of range, and F ion is 73-99.5% of range. Furthermore, OH concentration computed by C(cm-3) = alphax1019 from the absorption coefficient alpha of the absorption peak based on OH ion near the wavelength of 3 micrometers (cm-1) is 0.04-3x1019-/cm3 including OH ion. Diactinism ************** characterized by being a range.
[Claim 2] Glass according to claim 1 which displays at least one sort of alkali-metal ion chosen from Li, Na, and K by mol %, and contains it 5% or less.
[Claim 3] The manufacture method of ************** containing OH ion according to claim 1 which is the method of dissolving a raw materials for glass, cooling the obtained glass melt, and manufacturing glass, and is characterized by making dissolution atmosphere of the aforementioned raw materials for glass into the mixed-gas atmosphere of inert gas and a steam.
[Claim 4] The manufacture method of ************** containing OH ion according to claim 1 which is the method of dissolving a raw materials for glass, cooling the obtained glass melt, and manufacturing glass, and is characterized by using the mixture containing the compound which contains 5% or less of a hydroxide or water as a raw materials for glass.

[Translation done.]

* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] this invention relates to suitable diactinism ************** for the lens used for an ultraviolet linear light and ultraviolet-rays laser about 400nm or less, window part material, a mirror, prism, a filter, an etalon board, and the base material glass for optical fibers, and its manufacture method.
[0002]
[The technical problem which a Prior art and invention should solve] Progress of detailed-izing of LSI and high integration is very remarkable, and the element number per chip is already contained in the time of 1 million or more VLSIs in recent years. also in the optical lithography technology which draws a circuit pattern on a wafer in connection with this, the development progresses quickly, and 0.8 micrometers corresponding to the more detailed line breadth of 1 micrometer, for example, the line breadth corresponding to 1 M bit DRAM, and the 4M bit DRAM are developed And development of the lithography technology which can draw with the line breadth of 0.5 to 0.2 micrometer corresponding to submicron line breadth, for example, the range of 16-256 M bit DRAM, is hurried now. That to which it sees from steady progress of the latest optical system, the light source, a photoresist, etc., and optical lithography becomes in use too is presumed. However, when ultraviolet rays 400nm or less are used, with the lens using conventional optical glass, a light transmittance will fall [operating wavelength] rapidly from near 354nm (i line), generation of heat by the optical absorption will arise, and change and aberration of the focal position of a lens will arise. For this reason, although a quartz glass lens is used, an amendment of chromatic aberration poses a problem in that case. Moreover, since absorption by the optical induction defect arises when using the powerful homogeneous light like a KrF excimer laser (wavelength of 248nm), prolonged use cannot be performed. moreover -- although an alkali halogenide crystal and an alkaline-earth halogenide crystal have very good permeability on the property of the matter in other materials, since optical homogeneity of a single crystal is low and its chemical durability is not enough, either -- high performance and high energy -- in dense optical system, it is hard to change with optics, such as a lens Moreover, although a quartz fiber is used as a fiber for ultraviolet-rays transmission, since numerical aperture is not made greatly, new high numerical-aperture glass fiber is called for.
[0003] As good glass of a diactinism, ******** system glass is considered to excel in comparison in conventional optical glass with optical homogeneity. On this glass, since the fluorine which has a ultraviolet absorption in short wavelength rather than oxygen ion contains, it has the diactinism excellent farther than oxide glass. However, ************** containing a lot of fluorines has the low stability over devitrification, and it is very difficult to manufacture the glass which has optical homogeneity on a scale of industrial. As an ultraviolet-rays transparency little phosphoric acid content fluoride glass now P2 O5 0.5-8% and A12 O3 0.1-2% and BaO 0.5-7%, A1F3 29-42% MgF2 5-13% and CaF2 15-30.5%, SrF2 10-22% and BaF2 0-11% and BaCl2 ************** 0.5-16.5% and whose NaF are 0-7.5% is known [JP,2-283635,A]. However, although this glass was glass which contained fluorine ion in large quantities, in order to raise the stability over devitrification of glass, a lot of chloride ions were introduced, consequently sufficient permeability was not acquired in an ultraviolet-rays field with a wavelength of 350nm or less.
[0004] Then, the purpose of this invention is to offer ************** which shows permeability high enough also in an ultraviolet-rays field with a wavelength of 350nm or less, and has optical homogeneity, and its manufacture method.

[0005]
[Means for Solving the Problem] When many faults of the glass of the fluoride containing the above-mentioned conventional little phosphoric acid are analyzed, the decline in the ultraviolet-rays permeability of the glass at the time of removing a chloride ion is P-O-R (R=Mg, calcium, Sr, Na, Li, K) like phosphoric acid system glass.

** -- this invention persons thought that it was the shell to which combination [like] existed in glass structure Furthermore, it guessed that it became the greatest point to an improvement of the ultraviolet-rays permeability of glass to remove such combination from glass structure, and many things were examined. Consequently, it found out having the outstanding diactinism which does not have little OH dope ************** which replaced the P-O-R combination in glass structure by P-O-H combination until now, and having optical homogeneity by introducing little OH ion into the glass containing comparatively a small amount of phosphoric acid, and this invention was completed.
[0006] The rate of each aforementioned cation displays this invention by mol % as a cation which constitutes glass including P, aluminum, Y, Mg, calcium, Sr, and Ba. 0.15-20% of range and aluminum ion 22-40% of range, [P ion] Y ion as an anion which 7 - 16% of range and Ba ion are [4-15% of range, and Mg ion / 14-30% of range and Sr ion] 4-20% of ranges for 3-12% of range, and calcium ion, and constitutes glass The rate of each aforementioned anion displays by mol % including O ion and F ion. O ion is 0.5-27% of range, and F ion is 73-99.5% of range. Furthermore, OH ion is included. OH concentration computed by C(cm-3) = alphax1019 from the absorption coefficient alpha of the absorption peak based on OH ion near the wavelength of 3 micrometers (cm-1) is 0.04-3x1019/cm<SUP>3. It is related with diactinism ************** characterized by being a range.
[0007] It is the method of this invention dissolving a raw materials for glass, cooling the obtained glass melt, and furthermore manufacturing glass. The manufacture method of ************** containing OH ion of the aforementioned this invention characterized by making dissolution atmosphere of the aforementioned raw materials for glass into the mixed-gas atmosphere of inert gas and a steam, And it is the method of dissolving a raw materials for glass, cooling the obtained glass melt, and manufacturing glass, and is related with the manufacture method of ************** containing OH ion of the aforementioned this invention characterized by using the mixture containing the compound which contains 5% or less of a hydroxide or water as a raw materials for glass.
[0008] In addition, not only the ultraviolet-rays permeability of glass but the stability of ************** of this invention over devitrification of glass improved by having introduced OH ion. It is n as shown in drawing 1 (A1F4). By introducing P ion and OH ion into the fluoride glass which consists of the chain structure, strong hydrogen bond like P-O-H---F-A1- is formed, and it is n (A1F4). In order to join together in 3-dimensional chain structure, it is thought that crystallization of glass is suppressed. Each component of the glass of this invention is explained below.
[0009] P ion is a component which works as a glass forming oxide and increases the stability over stabilization, i.e., devitrification, of glass structure. Moreover, P ion is an indispensable component in order to raise chemical durability. Furthermore, since P ion has the property preferentially combined with OH ion compared with other cations, most OH ion in glass is combined like P-O-H by carrying out fluoride-glass introduction of the P ion. It was checked in the experiment of this invention persons that such combination contributes to improvement in the ultraviolet-rays permeability of glass compared with combination like A1-O-H. However, if P ion increases more than 20% as a component of glass, since combination like P-O-R to which the permeability of ultraviolet rays is reduced will increase relatively, the ultraviolet-rays permeability of the obtained glass gets worse. On the other hand, if there are few contents of P ion than 0.5%, the stability over devitrification of glass will become bad, and chemical durability will also fall. Therefore, it is suitable for the composition range of P ion that it is 0.5-20% of range. Especially, it is desirable that it is 1-19% of range.
[0010] A1 ion is very important also as a component which raises stabilization of glass structure, and the viscosity of a glass melt with P ion also as a component which gives the property of the high ultraviolet-rays permeability of glass, and contributes to improvement in chemical durability. In order to give the optical property of high ultraviolet-rays permeability to glass, and to raise the stability over devitrification, 22% or more is required. However, if it exceeds 40%, it will become easy to devitrify conversely. Therefore, it is suitable for the composition range of A1 ion that it is 22-40% of range. Especially, it is desirable that it is 23-38% of range.
[0011] Y ion is a component which contributes to improvement in stability, or the refractive index and chemical durability to devitrification of glass. However, since it will on the contrary become easy to devitrify if it introduces exceeding the proper quantity range, it is suitable that it is 4-15% of range. Especially, it is desirable that it is 5-13% of range.
[0012] Mg ion is a component very useful for raising the ultraviolet-rays permeability of glass. However, since the stability over devitrification of glass will become low if it exceeds 12%, and the elevated-temperature solubility of glass will become bad if fewer than 3%, 3-12% of range is suitable. Especially, it is desirable that it is 4-10% of range.
[0013] calcium ion is a component effective in extending the stable vitrification range to devitrification while giving high ultraviolet-rays permeability to glass. However, since it exceeds 30% or the stability over devitrification of glass falls at less than 14%, it is suitable that it is 14-30% of range. Especially, it is desirable that it is 14.5-28% of range.
[0014] Each comparatively big ion of the atomic number like Sr and Ba is a component introduced in order to raise the

stability and the refractive index to devitrification of glass in alkaline earth metal. However, if the amount of introduction of Sr ion and Ba ion exceeds 16% and 20%, respectively, to the stability over devitrification of glass getting worse, at 7% and less than 4%, elevated-temperature solubility will become bad and sufficiently stable glass will not be obtained, either. Therefore, it is suitable for the amount of introduction of Sr ion and Ba ion respectively that it is 7-16% and 4-20% of range. It is desirable that Sr ion is 8-15% and especially Ba ion is 4-19% of range.

[0015] Although it is not an indispensable component, alkali-metal ion is a very useful component, when adjusting the fusion nature and transition temperature of glass. However, if it exceeds 5%, the stability over devitrification of glass will get worse and chemical durability will also fall. Therefore, it is suitable that it is 3.5% or less preferably 5% or less.

[0016] The oxygen ion in the anion which constitutes glass is a component which raises the stability over devitrification of glass. To the effect that oxygen ion suppresses the devitrification inclination of glass at less than 0.5% falling, if it exceeds 27%, a high diactinism will no longer be obtained. Therefore, it is appropriate for the rate of oxygen ion to consider as 0.5-27% of range. Especially, 1-26% of range is desirable.

[0017] The fluorine ion in the anion which constitutes glass is the component which can raise the ultraviolet-rays permeability of glass by making it contain in large quantities. To ultraviolet-rays permeability with fluorine ion high at less than 73% not being obtained, if it exceeds 99.5%, sufficiently stable glass will no longer be obtained. Therefore, it is appropriate for the rate of fluorine ion to consider as 73-99.5% of range. Especially, 74-99% of range is desirable.

[0018] For the glass of this invention, in addition to the above-mentioned component, OH concentration computed by C(cm-3) = alphax1019 from the absorption coefficient alpha of the absorption peak based on OH ion near the wavelength of 3 micrometers (cm-1) is 0.04-3x1019-/cm3, including OH ion. It is the feature that it is a range. It is very effective in being able to extend the vitrification range by introducing OH ion of the specified quantity into **************, and raising the stability over devitrification. Although introduced OH ion has few numbers as shown in drawing 1 , they are much (A1F4) n at strong hydrogen bond like (P-O-H---F-A1-F). The chain structure is connected and it is thought that glass structure is strengthened. The content of OH ion of glass is 0.04x1019-/cm3. Since there is no effect in the increase in the stability over devitrification at the following and the diactinism of glass also gets worse, it is 0.04x1019-/cm3. It is necessary to introduce the above OH ion. Moreover, since it is the component introduced in order that each OH ion may form combination like P ion and P-O-H---F, it is necessary to increase the amount of introduction of OH ion with the increase in a phosphoric acid content. This is for increasing the ultraviolet-rays permeability of glass. However, the content of OH ion is 3x1019-/cm3. If it exceeds, the stability over devitrification of glass will get worse. Therefore, 3x1019cm3 Considering as the following is appropriate. Especially, it is 3 0.05-2.5x1019cm. The range and a bird clapper are desirable.

[0019] In order to raise the stability over devitrification of glass, it is appropriate to introduce OH ion of a proper quantity according to the content of phosphoric acid so that drawing 1 may also show as mentioned above. For example, as shown in the photograph of drawing 2 , the glass which does not contain OH ion obtained by dissolving in argon atmosphere was devitrified. On the other hand, when it dissolves in the mixed-gas atmosphere of an argon and a steam, it is only 0.087x1019-/cm3. Transparent glass without a crystal is obtained by making OH ion mix from dissolution atmosphere.

[0020] ************** containing OH ion of this invention is the method of dissolving a raw materials for glass, cooling the obtained glass melt, and manufacturing glass, and can be manufactured by the method using the mixture containing the compound which contains water as 5% or less of a hydroxide or water of crystallization etc. as the method of making dissolution atmosphere of the (1) aforementioned raw materials for glass the mixed-gas atmosphere of inert gas and a steam, or (2) raw materials for glasses. The method of the above (1) is a method of making OH ion mixing in glass using the reaction of the steam in dissolution atmosphere, and a glass melt. As inert gas, gas, such as nitrogen, an argon, helium, and neon, can be used, for example. You pass these inert gas to the scrubbing bottle containing water, and it is made to be saturated with the steam in a washing bottle, after obtaining a certain amount of steam partial pressure, a glass fusion furnace is supplied, and it considers as the atmosphere of the glass dissolution. For example, it is shown as a process of the steam introduction of the situation to a fusion furnace to drawing 3 . The amount of introduction of a steam is adjusted at the temperature of the water in the washing bottle shown in drawing 3 . That is, the content of OH ion in glass can be adjusted by adjusting the steam partial pressure of fusion furnace atmosphere at the water temperature in a scrubbing bottle. In this method, what mixed what is usually used as a raw materials for glass so that it might become desired composition except for OH ion can be used for a raw materials for glass. However, when not the thing that means that the compound containing a hydroxide or water of crystallization cannot be used but the compound which contains a hydroxide and water of crystallization in some raw materials is used, the glass containing OH ion of the amount of requests can be manufactured by adjusting the reaction of a steam

and a glass melt suitably.

[0021] The method of the above (2) is a method using the mixture containing the compound which contains 5% or less of a hydroxide or water as a raw materials for glass. That is, ************** of this invention which introduced OH ion can be manufactured by using the mixture containing the compound containing water, such as an oxide which contains the hydroxide of H3 PO4, A1(OH)3, and alkaline earth metal the hydroxide of alkali metal, etc. and water of crystallization so that desired OH ion may be included, as a raw materials for glass in addition to compounds, such as the fluoride and oxide which are the usual raw materials for glass, phosphate, a carbonate, and a nitrate. However, if the stability over the devitrification nature of glass is taken into consideration, it is appropriate to make the addition of each compound containing OH below into 5% (mol %). Especially, it is desirable that it is 4.5% or less.

[0022] As a crucible used in case glass is manufactured, although the product made from GURASHII carbon is desirable, it is also possible to use a platinum crucible. However, when using a platinum crucible, the cautions which avoid mixing of platinum inclusions are required for glass. Moreover, by the method of the above (1), inert gas is used by the method of the above (2), using the mixed gas of inert gas and a steam as a dissolution atmosphere of glass. Inert gas is the aforementioned thing. It is for preventing the fluorine in glass, and volatilization of OH by using inert gas, and is also for making OH ion mix in glass from dissolution atmosphere.

[0023]

[Effect of the Invention] OH dope ************** of this invention can have the outstanding diactinism which is not until now, and can obtain it comparatively stably also as glass. Therefore, production on a industrial scale is possible and they are quartz glass and CaF2. It is very promising as an optical material replaced with a crystal. Furthermore, it is promising also as an optic used for an optical instrument also as a base material of the fiber for an ultraviolet linear light and visible optical transmissions. It is useful to the creation of the fiber for ultraviolet-rays transmission which has numerical aperture large [0.2 or more] especially.

[0024]

[Example] Hereafter, although this invention is explained further, this invention is not limited to these examples. The rate of a cation and an anion was shown for glass composition of an example in one to example 36 Table 1 - 3, and the rate of the various compounds corresponding to the composition shown in Table 1 - 3 was shown in Table 4 - 6 by mol %. As a start raw material at the time of dissolving these glass A1(PO3) 3, Mg (PO3)2, and calcium (PO3)2, Sr (PO3)2, Ba (PO3)2, H3 PO4, and A1(OH)3, Mg -- (-- OH --) -- two -- calcium -- (-- OH --) -- two -- Sr -- (-- OH --) -- two -- Ba -- (-- OH --) -- two -- A -- one -- F -- three -- YF -- three -- MgF -- two -- CaF -- two -- SrF -- two -- BaF -- two -- NaF -- LiF -- and -- KF -- etc. -- having used . It ****(ed) 50-100g in predetermined proportion shown in Tables 4-6, it mixed enough, and these raw materials were accomplished with the preparation raw material. The obtained preparation raw material was paid to the carbon crucible, and glass was dissolved in the mixed-gas atmosphere of an argon and a steam by 950-1100 degrees C for 1 to 2 hours. After fusion, it cooled radiationally to the room temperature, putting a glass melt into a carbon crucible, and glass was obtained. The crystal which the obtained glass is transparent and colorless and can be observed with an optical microscope did not deposit.

[0025] Mixture (or the both) of the compound containing the hydroxide and/or water of crystallization of a steam to introduction or a raw material to glass dissolution atmosphere performed introduction of OH ion to the inside of glass. About introduction of a steam, argon gas was saturated with the steam in a washing bottle, after obtaining a certain amount of steam partial pressure, this mixed gas was supplied to the fusion furnace, and it considered as the atmosphere of the glass dissolution. The steam partial pressure of fusion furnace atmosphere was adjusted at the temperature of the water in the washing bottle shown in drawing 3 , and adjusted the content of OH ion in glass through this. For example, the concentration of OH ion in the glass of examples 26, 27, and 28 which dissolved in a mixed atmosphere of 25 and the steam partial pressure which made temperature of the water of a washing bottle 45 or 85 degrees C is 0.21, 0.46, and 0.88x1019-/cm3, respectively. It became. In addition, examples 1, 2, 4, 7, 11, 12, 13, 14, 15, 16, 17, 18, 20, 23, 24, 26, 27, 29, 34, 35, and 36 introduced OH ion by introduction of the steam to the inside of dissolution atmosphere. Moreover, examples 30 and 32 introduced OH ion by mixture of the hydroxide to a raw material. Furthermore, examples 3, 5, 6, 8, 9, 10, 19, 21, and 22 introduced OH ion by introduction of the steam to the inside of dissolution atmosphere, and mixture of the hydroxide to a raw material. OH ion content of each glass is shown in Tables 1-3.

[0026]

[Table 1]

実施例番号	1	2	3	4	5	6	7	8	9	10	11	12
陽イオン%												
Pイオン	0.50	0.50	0.50	1.00	1.00	1.00	2.99	2.99	2.99	2.99	2.99	2.99
Alイオン	34.50	34.50	34.50	35.54	34.85	36.05	36.52	36.52	36.52	37.52	36.52	30.35
Yイオン	9.77	9.77	9.77	10.21	10.79	9.59	9.00	9.00	9.00	8.85	9.00	13.69
Mgイオン	7.06	7.06	7.06	6.81	5.63	5.63	6.59	6.59	6.08	5.97	11.69	4.73
Caイオン	25.33	25.33	25.33	24.42	24.92	24.92	23.61	23.61	21.79	25.38	18.51	19.82
Srイオン	12.39	12.39	12.39	11.95	12.19	12.19	11.55	11.55	10.66	10.47	11.55	13.75
Baイオン	10.45	10.45	10.45	10.07	10.62	10.62	9.74	9.74	12.97	8.83	9.74	14.68
Liイオン	---	---	---	---	---	---	---	---	---	---	---	---
Naイオン	---	---	---	---	---	---	---	---	---	---	---	---
Kイオン	---	---	---	---	---	---	---	---	---	---	---	---
陰イオン%												
Oイオン	0.62	0.62	0.62	1.22	1.22	1.22	3.65	3.65	3.65	3.64	3.65	3.67
Fイオン	99.38	99.38	99.38	98.78	98.78	98.78	96.35	96.35	96.35	96.36	96.35	96.33
OH($10^{19}/cm^3$)	0.052	0.087	0.32	0.11	0.27	0.51	0.15	0.36	0.68	1.09	0.16	0.15
透過率(200nm)	86.0	86.5	87.0	85.5	86.0	86.0	85.0	86.0	84.5	83.5	85.5	86.0

[0027]
[Table 2]

実施例番号	13	14	15	16	17	18	19	20	21	22	23	24
陽イオン%												
Pイオン	2.99	2.99	2.99	2.99	2.99	4.14	4.14	4.98	4.98	4.98	4.98	4.98
Alイオン	38.32	35.33	35.33	35.33	31.02	35.48	35.48	34.92	34.92	34.92	34.92	34.93
Yイオン	5.72	8.71	8.71	8.71	14.50	8.65	8.65	8.61	8.61	8.61	8.61	8.61
Mgイオン	4.73	5.15	3.45	10.06	6.59	6.62	6.62	6.59	6.59	6.59	6.09	6.09
Caイオン	19.82	16.83	28.77	26.30	23.61	23.73	23.73	23.61	23.61	23.61	23.61	23.61
Srイオン	13.75	14.99	10.04	11.89	11.55	11.61	11.61	11.55	11.55	11.55	11.55	11.55
Baイオン	14.68	16.01	10.72	4.74	9.74	9.79	9.79	9.74	9.74	9.74	9.24	8.74
Liイオン	—	—	—	—	—	—	—	—	—	—	1.00	—
Naイオン	—	—	—	—	—	—	—	—	—	—	—	1.50
Kイオン	—	—	—	—	—	—	—	—	—	—	—	—
陰イオン%												
Oイオン	3.67	3.67	3.67	3.67	3.67	5.09	5.09	6.13	6.13	6.13	6.14	6.15
Fイオン	96.33	96.33	96.33	96.33	96.33	94.91	94.91	93.87	93.87	93.87	93.86	93.85
OH(10^{17}/cm^3)	0.15	0.16	0.17	0.15	0.15	0.18	0.41	0.19	0.41	0.92	0.18	0.19
透過率(200nm)	86.0	86.0	86.0	86.0	86.0	—	—	84.0	84.0	83.0	84.0	84.0

[0028]
[Table 3]

実施例番号	25	26	27	28	29	30	31	32	33	34	35	36
陽イオン%												
Pイオン	4.98	6.97	6.97	6.97	10.00	10.00	10.00	10.00	10.00	12.00	15.00	18.00
Alイオン	34.93	33.33	33.33	33.33	31.30	31.30	31.30	31.30	31.30	29.29	26.25	23.52
Yイオン	8.61	8.21	8.21	8.21	6.93	6.93	6.93	6.93	6.93	7.73	7.93	7.93
Mgイオン	6.09	6.59	6.59	6.59	6.32	6.32	6.32	4.32	4.32	3.78	3.78	3.62
Caイオン	23.61	23.61	23.61	23.61	22.73	22.73	22.73	21.73	21.73	16.62	14.86	14.86
Srイオン	11.05	11.55	11.55	11.55	12.91	12.91	12.91	11.91	11.91	10.41	9.71	10.70
Baイオン	9.24	9.74	9.74	9.74	9.79	9.79	9.79	9.29	9.29	18.47	18.47	16.87
Liイオン	—	—	—	—	—	—	—	—	—	—	—	—
Naイオン	—	—	—	—	—	—	—	4.50	—	1.70	4.00	4.50
Kイオン	1.5	—	—	—	—	—	—	—	4.50	—	—	—
陰イオン%												
Oイオン	6.15	8.65	8.65	8.65	12.62	12.62	12.62	12.87	12.87	15.30	19.55	23.79
Fイオン	93.85	91.35	91.35	91.35	87.38	87.38	87.38	87.13	87.13	84.70	80.45	76.21
OH(10^{17}/cm^3)	0.18	0.21	0.46	0.88	0.23	0.64	2.84	0.74	0.23	0.27	0.31	0.36
透過率(200nm)	84.0	83.0	83.5	82.5	82.0	82.0	79.5	81.5	82.0	81.0	78.5	76.0

[0029]
[Table 4]

実施例番号	1	2	3	4	5	6	7	8	9	10	11	12
PO2.5	0.50	0.50	0.50	1.00	1.00	1.00	2.99	2.99	2.99	2.99	2.99	2.99
AlO1.5	0.167	0.167	0.167	0.334	0.334	0.334	0.995	0.995	0.995	0.995	0.995	0.995
BaO	—	—	—	—	—	—	—	—	—	—	—	—
AlF3	34.33	34.33	34.33	35.21	34.52	35.72	35.52	35.52	35.52	34.02	35.52	29.35
YF3	9.77	9.77	9.77	10.21	10.79	9.59	9.00	9.00	9.00	8.85	9.00	13.69
MgF2	7.06	7.06	7.06	6.81	5.63	5.63	6.59	6.59	6.08	5.97	11.69	4.73
CaF2	25.33	25.33	25.33	24.42	24.92	24.92	23.61	23.61	21.79	25.38	18.51	19.82
SrF2	12.39	12.39	12.39	11.95	12.19	12.19	11.55	11.55	10.66	10.47	11.55	13.75
BaF2	10.45	9.95	9.45	10.07	10.12	9.62	9.74	9.24	11.97	8.83	9.74	14.68
LiF	—	—	—	—	—	—	—	—	—	—	—	—
NaF	—	—	—	—	—	—	—	—	—	—	—	—
KF	—	—	—	—	—	—	—	—	—	—	—	—
Al(OH)3	—	—	—	—	—	—	—	—	—	1.50	—	—
Ba(OH)2	—	—	1.00	—	0.50	1.00	—	0.50	1.00	—	—	—
Na(OH)	—	—	—	—	—	—	—	—	—	—	—	—

[0030]
[Table 5]

実施例番号	13	14	15	16	17	18	19	20	21	22	23	24
PO2.5	2.99	2.99	2.99	2.99	2.99	4.14	4.14	4.98	4.98	4.98	4.98	4.98
AlO1.5	0.995	0.995	34.33	0.995	0.995	1.38	1.38	0.995	0.995	0.995	0.995	0.995
BaO	—	—	—	—	—	—	—	0.995	0.995	0.995	0.995	0.995
AlF3	37.32	34.33	34.33	34.33	31.02	34.10	34.10	33.92	33.92	33.92	33.92	33.93
YF3	5.72	8.71	8.71	8.71	14.50	8.65	8.65	8.61	8.61	8.61	8.61	8.61
MgF2	4.73	5.15	3.45	10.06	6.59	6.62	6.62	6.59	6.59	6.59	6.09	6.09
CaF2	19.82	16.83	28.77	26.30	23.61	23.73	23.73	23.61	23.61	23.61	23.61	23.61
SrF2	13.75	14.99	10.04	11.89	11.55	11.61	11.61	11.55	11.55	11.55	11.55	11.55
BaF2	14.68	16.01	10.72	4.74	9.74	9.79	9.29	8.75	8.25	7.75	8.25	7.75
LiF	—	—	—	—	—	—	—	—	—	—	1.00	—
NaF	—	—	—	—	—	—	—	—	—	—	—	1.50
KF	—	—	—	—	—	—	—	—	—	—	—	—
Al(OH)3	—	—	—	—	—	—	—	—	—	—	—	—
Ba(OH)2	—	—	—	—	—	—	0.50	—	0.50	1.00	—	—
Na(OH)	—	—	—	—	—	—	—	—	—		—	—

[0031]
[Table 6]

実施例番号	25	26	27	28	29	30	31	32	33	34	35	36
PO2.5	4.98	6.97	6.97	6.97	10.00	10.00	10.00	10.00	10.00	12.00	15.00	18.00
AlO1.5	0.995	2.32	2.32	2.32	3.34	3.34	3.34	3.34	3.34	4.00	5.00	5.00
BaO	0.995	—	—	—	—	—	—	—	—	—	—	—
AlF3	33.93	31.01	31.01	30.51	27.96	27.96	23.96	27.96	27.96	25.29	21.25	17.52
YF3	8.61	8.21	8.21	8.21	6.93	6.93	6.93	6.93	6.93	7.73	7.93	7.93
MgF2	6.09	6.59	6.59	6.59	6.32	6.32	6.32	4.32	4.32	3.78	3.78	3.62
CaF2	23.61	23.61	23.61	23.61	22.73	22.73	22.73	21.73	21.73	16.62	14.86	14.86
SrF2	11.05	11.55	11.55	11.55	12.91	12.91	12.91	11.91	11.91	10.41	9.71	10.70
BaF2	8.25	9.74	9.24	9.74	9.79	9.19	9.79	9.29	9.29	18.47	18.47	16.87
LiF	—	—	—	—	—	—	—	—	—	—	—	—
NaF	—	—	—	—	—	—	—	3.00	—	1.70	4.00	4.50
KF	1.50	—	—	—	—	—	—	—	4.50	—	—	—
Al(OH)3	—	—	—	0.50	—	—	4.00	—	—	—	—	—
Ba(OH)2	—	—	—	—	—	0.60	—	—	—	—	—	—
Na(OH)	—	—	—	—	—	—	—	1.50	—	—	—	—

[0032] The JEOL -330 type spectrophotometer and the Japanese duty light VALOR-III type infrared spectrophotometer performed measurement of the infrared spectrum of glass, and a ultraviolet spectrum using sample glass with a thickness of 10mm, respectively. The fixed quantity of the concentration of OH ion in glass was carried out using the infrared absorption spectrum of glass by the following formula (see Journal of Non-Crystalline Solids and the reference of 163 (1993)p74-80).
OH concentration (cm-3) =alpha(OH) x1019 -- alpha (OH) of an absorption coefficient and (cm-1) are calculable by the following formula from an absorption spectrum here
alpha(OH) =(1-/LO) xLn (IO/ID)
It is LO here. The thickness of a sample, and IO The highest permeability (permeability with a wavelength of 1400nm is usually used) of a sample, and ID It is the permeability in the wavelength used as the absorption peak of OH ion in the wavelength 3000-3200nm range.
[0033] The ultraviolet-rays transparency spectrum of the glass (example of comparison) of this composition which dissolved in drawing 4 in the argon gas atmosphere which carried out the glass of an example 7 which dissolved in the mixed-gas atmosphere of the (A) argon and a steam, and (B) dryness was shown. Drawing 4 shows that the ultraviolet-rays permeability of the glass of this invention which dissolved in the atmosphere containing a steam is higher than that of the glass of the example of comparison which dissolved in dryness argon gas atmosphere. Moreover, in order to compare with quartz glass, the ultraviolet-rays transparency spectrum of commercial Suprasil-P20 quartz glass and the glass of an example 14 was shown in drawing 5 . Drawing 5 shows clearly having permeability somewhat higher than it with the glass of this invention of the same grade as quartz glass in the ultraviolet-rays field of 200 to 400 nm wavelength or. The diactinism about the glass of the example of further others is shown in Tables 1-3. The glass of this invention is expected from the above example as optical materials, such as a lens for ultraviolet linear lights of 200-400nm wavelength range, aperture material, a mirror, and a filter, or a base material for ultraviolet linear-light transmission fibers.

[Translation done.]